

Determination of melting temperatures of crystalline materials using differential thermal analysis

DIN
51 004

ICS 71.040.40

Thermische Analyse (TA); Bestimmung der Schmelztemperaturen kristalliner Stoffe mit der Differenzthermoanalyse (DTA)

In keeping with current practice in standards published by the International Organization for Standardization (ISO), a comma has been used throughout as the decimal marker.

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1 Scope and field of application

This standard specifies methods of determining the melting temperatures of crystalline materials using differential thermal analysis (DTA). The determination of the purity of eutectic mixtures by observing their melting behaviour is also covered.

The methods described here are analogous to those used to determine other first order transition temperatures (e.g. recrystallization temperatures, solid-solid transition temperatures, and phase transition temperatures of liquid crystals) and may involve the use of differential scanning calorimetry (DSC).

2 Concepts

See DIN 51 005 and DIN 51 007 for general concepts relating to DTA.

2.1 Melting (also referred to as fusion) is a thermal process by which a material changes from a crystalline to a liquid form without undergoing any chemical changes; this includes the transition from the solid crystalline state to the liquid crystalline state. Such a transition is accompanied by a positive enthalpy change, producing an endothermic peak.

NOTE: As defined above, 'melting' does not encompass the softening of amorphous solids.

2.2 The melting temperature of pure substances is the exact temperature at which, at a given pressure, the solid and liquid phases are in equilibrium regardless of their quantity ratio. The relationship between the melting temperature and pressure is plotted as a curve in a pressure-temperature diagram.

NOTE: It should be noted that equilibrium conditions cannot be maintained during dynamic testing as described in this standard.

For the purposes of this standard, the **melting point** is the melting temperature obtained at standard pressure (1013 hPa).

2.3 For mixtures or impure substances, a well-defined melting temperature is not normally observed. In these cases, the **onset temperature** indicates the temperature at which melting begins, while the temperature at which the transition is completed is referred to as the **end temperature**.

2.4 The melting range is the melting temperature range between the onset and end temperatures.

NOTE: Values for melting temperatures and temperature ranges obtained during dynamic testing will differ from those obtained under equilibrium conditions.

2.5 Polymorphous substances exist in two or more crystal forms; in this case, a separate pressure-temperature curve for each modification should be plotted.

When testing polymorphous materials using a dynamic method, the transition from one solid phase to another may not take place, due to the 'lag phenomenon' (i.e. a delay in the formation of crystal nuclei). In this case, melting will begin at a lower temperature than that observed under equilibrium conditions.

2.6 Eutectic purity refers to the concentration of the main component in a binary eutectic system. For eutectic mixtures, the melting point is referred to as the **eutectic temperature**, or the temperature at which the main component begins to melt.

Continued on pages 2 to 4.

3 Sampling and specimen preparation

See DIN 51 007 for general sampling and specimen preparation procedures, and ISO 2859-1 for sampling plans.

Sampling shall be carried out in such a manner that the specimen is homogeneous and representative of the material being tested and the requirements of the instruments used are met. To this end, mixing, grinding to reduce particle size, sample division or other techniques may be necessary, although a chemical alteration of the specimen (e.g. an increase in its chemical potential) should be avoided.

Specimens should be conditioned in a DIN 50 014-20/65-1 standard atmosphere. However, since conditioning parameters will also affect melting behaviour, materials which are sensitive to light, oxidation and other physical and chemical reactions (e.g. water absorption or evaporation, solvent dissipation, absorption of CO_2) should be conditioned under appropriate conditions (e.g. in an inert atmosphere).

4 Apparatus

See DIN 51 007 for requirements.

5 Calibration

Calibration involves the comparison of recorded values with corresponding known values using standard materials.

Calibrate the instrument's temperature axis and heat flow axis, and instruments measuring eutectic purity as specified in DIN 51 007 using the standard materials listed there or any other appropriate standards. Choose standard materials which have thermal properties equivalent to those of the specimen, which do not decompose when heated to the melting point, and which do not undergo any chemical changes in the temperature range being measured.

Several organisations*) publish lists of recommended standards, including organic standard materials, for temperature and heat flow calibration. For purity determination, standards with a concentration identical to that of the materials being tested shall be used.

6 Procedures and evaluation

Other methods than those described in this standard may be used (e.g. the capillary tube method or thermomicroscopic method(s) for determining melting temperatures, and chromatography, spectroscopy or cyroscopy for determining purity).

6.1 Determining melting temperatures

6.1.1 Procedure

After sampling and preparing the specimen as specified in clause 3, set up the apparatus according to the requirements set down in DIN 51 007 and under the same conditions as were used for calibration.

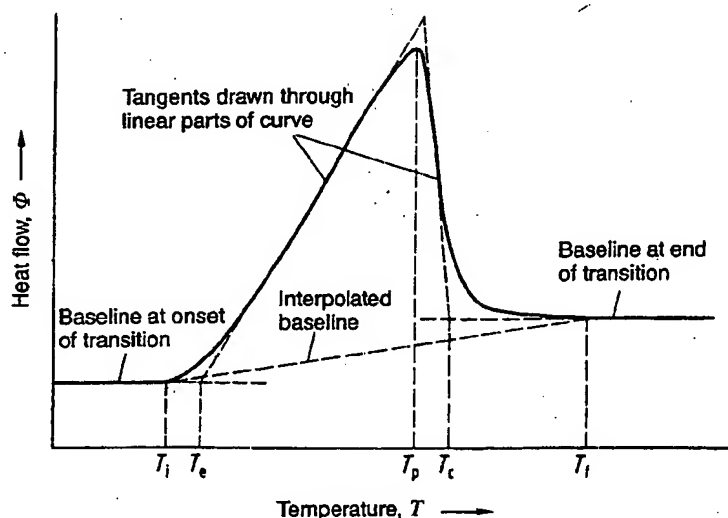


Figure 1: Characteristic melting endotherm

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GEFTA (Gesellschaft für Thermische Analyse (German Society for Thermal Analysis)), Freiburg, Germany

WHO (World Health Organization), CH-1211 Genève 27, Switzerland

NPL (National Physical Laboratory), Teddington, Middlesex TW 11 OLW, United Kingdom

LGC (Laboratory of the Government Chemist), Teddington, Middlesex TW 11 OLW, United Kingdom

NIST (National Institute of Standards and Technology), Building 220, Gaithersburg, MD 20899, USA

6.1.2 Requirements for DTA curves

If testing produces a clear endotherm, the peak can be immediately evaluated. If curves are difficult to interpret, altering test and specimen parameters or even the initial mass of the specimen may be necessary to produce a clear peak.

DTA curves in which the melting process is not readily identifiable (e.g. glass transition curves for amorphous materials, or curves in which decomposition sets in before melting has begun) cannot be evaluated. However, curves which exhibit a clear onset of the transition before decomposition has begun can still be evaluated as described in subclause 6.1.3.

6.1.3 Evaluation

See DIN 51 005 for general concepts.

Melting produces an endothermic peak which is plotted in the positive coordinate plane as a function of heat flow and temperature (figure 1^{*)}), where

T_i is the onset temperature;

T_e is the extrapolated onset temperature;

T_p is the peak temperature;

T_c is the extrapolated end temperature;

T_f is the end temperature.

See DIN 51 007 for two methods of interpolating the baseline. In most cases, the interpolated baseline can also be used to accurately determine the extrapolated onset and end temperatures.

The tangents drawn through the linear portions of the curve can be either regression lines or inflectional tangents. The difference between the two types of tangents is not relevant to calibration, since the difference between the results they produce is smaller than the repeatability standard deviation.

If the onset temperature cannot be accurately determined, the peak temperature can be taken as the melting temperature, although it should be borne in mind that this temperature is highly dependent on test parameters such as the initial mass of the specimen or the heating rate used.

The temperature range between the onset and end temperatures gives the melting range.

Curves are normally evaluated by the analyser or calorimeter automatically. Nevertheless, it must be kept in mind that the determination of characteristic temperatures is open to interpretation.

6.2 Determining eutectic purity

Thermal analysis can be used to determine the purity of a binary eutectic system, although mixtures comprising mixed crystals or components which form compounds cannot be analysed by this method.

The presence of impurities which are insoluble will not affect results and do not influence the determination of the purity of the mixture. Where the amount of substance of the second component, x_2 , is above 0.01 and below 0.03, an uncertainty of measurement of 20 % is to be expected.

DTA is also instrumental in determining whether a mixture is eutectic or not.

6.2.1 Procedure

Place the finely ground specimen, which should be as small as possible, in a sealed specimen holder and heat it to a temperature above the melting temperature at a high heating rate (e.g. 10 °C/min). Then, cool the specimen quickly until it fully crystallizes below the defined eutectic temperature. Heat the specimen again at a heating rate of 1 °C/min and record the result.

6.2.2 Evaluation

According to Van't Hoff's law, the purity of an eutectic mixture can be determined by calculating the melting temperature of the liquid mixture, T_F , obtained after heating as a function of the reciprocal of the melted portion, $1/F$:

$$T_F = T_{fus} - RT_{fus}^2 / \Delta_{fus} H \cdot x_2^* \cdot 1/F$$

where

T_E is the melting temperature of the liquid mixture (refer to instrument manufacturer's instructions to determine this temperature);

T_{fus} is the melting temperature of the (pure) main component;

R is the gas constant;

$\Delta_{fus} H$ is the molar heat of fusion of the main component;

x_2^* is the amount of the impurity in the original mixture;

F is the amount of the specimen which melted at T_F (this is determined by taking the ratio of the peak area at T_F to the total peak area after having compensated for signal noise according to the manufacturer's instructions).

The function $T_F = f(1/F)$ derived from this equation is then to be linearized by multiple linear regression, the analytical three-point method, or successive addition of an extra area taken from another part of the recorded peak. However, this linearization is only possible within a limited range (e.g. for $1/F$ from 2 to 10).

This linearized function gives T_{fus} , while x_2^* is taken from the slope of the straight line.

NOTE: Most DTA equipment are equipped with a computer programmed to automatically evaluate results. The algorithms and parameters for these calculations are thus predetermined and cannot be adjusted to the problem at hand through calibration.

7 Test report

Test reports shall refer to this standard and include the following information:

- complete identification of material used;
- thermal history, sampling, conditioning and preparation of specimen and sample material;

^{*)} Translator's note: This means of plotting DTA/DSC curves is common practice in Germany, in accordance with the recommendations of the ICTA and GEFTA. However, as the Anglo-American literature shows, most computer programs on the market produce curves for which the reverse is true, i.e. melting endotherms are plotted in the negative coordinate plane, crystallization exotherms in the positive coordinate plane (cf. ISO 3146: 1985, ASTM E 793-85).

- c) initial mass of specimens;
- d) description of equipment (DTA analyzer or DSC calorimeter) used;
- e) material and dimensions of sample holders;
- f) atmospheric conditions;
- g) temperature programme parameters, including initial and end temperatures, and heating rates;
- h) temperature, temperature difference and/or heat flow difference measurement ranges;
- i) test results and evaluation parameters, including integration limits, baseline construction, values obtained by calculation, calibration values, and algorithms used in evaluation;
- j) error analysis, where relevant.

Standards referred to

- DIN 50 014 Artificial climates in technical applications; standard atmospheres
- DIN 51 005 Thermal analysis; concepts
- DIN 51 007 General principles of differential thermal analysis
- ISO 2859-1:1989 Sampling procedures for inspection by attributes; sampling plans indexed by acceptable quality level (AQL) for lot-by-lot inspection

Explanatory notes

This standard has been prepared by Technical Committee *Thermische Analyse* of the *Normenausschuß Materialprüfung* (Materials Testing Standards Committee).

International Patent Classification

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